SPAWAR
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San Diego

TECHNICAL REPORT 1898
June 2003

Coastal Contaminant Migration Monitoring Technology Review

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ADMINISTRATIVE INFORMATION

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SB

Executive Summary

The U.S. Navy is identifying, assessing, and remediating a large number of terrestrial hazardous waste sites. Many sites are located adjacent to harbors, bays, estuaries, wetlands, and other coastal environments. Approximately one-third of all U.S. Navy landfills have groundwater infiltrating the waste, and as a result the Navy must determine if contaminants from these sites are migrating into marine systems at levels that pose a threat to the environment.

Complex physical and geochemical processes arising from interactions between seawater, groundwater, soils, sediments, and contaminants affect the transport and mobility of contaminants from the waste site. As a result of chemical differences between groundwater and seawater, groundwater exchange between the waste site and the adjacent coastal water bodies is a likely migration pathway for dissolved nutrients and contaminants, particularly in areas with strong tidal influence. In coastal areas, tidal mixing zones may form from the movement of seawater into the aquifer (Figure 1, page 2). The tidally mixed zone may be important in estimating the amount of groundwater extracted due to a process referred to as tidal pumping (Moore, 1996). This is when higher density seawater mixes with groundwater at high tide, and then as the tide recedes, the mixture of seawater and groundwater is drawn out into the coastal waters. Because this process repeats at every tidal cycle, appreciable volumes of groundwater can be extracted over time. Increasingly, groundwater is recognized as a potentially significant, although poorly quantified, source of nutrients and contaminant materials to coastal ecosystems.

These problems are generally evaluated by making hydraulic head measurements in shore-side wells and/or numerical models that provide theoretical predictions of flow and contaminant migration. However, these models are of limited use in areas adjacent to marine systems where tides, waves, and strong density gradients make it difficult to establish boundary conditions. Few techniques are available to verify if the model predictions are accurate.

Growing evidence suggests that submarine groundwater discharge may represent an important migration pathway for natural and anthropogenic constituents entering coastal waters (Lendvay et al., 1998). To address this issue, a series of technologies were investigated for their applicability toward direct quantification of coastal contaminant migration via groundwater. Candidate technologies were divided into two categories: (1) technologies for quantifying groundwater flow to coastal waters, and (2) technologies for detecting contaminants in the groundwater–coastal water exchange zone.

The technologies evaluated for quantifying groundwater flow to coastal waters include seepage meters, thermal gradient flow meters, piezometers, thermal infrared aerial imagery, tracer injection, a colloidal borescope, and natural geochemical tracers.

The technologies for detecting contaminants in the groundwater–coastal water exchange zone include porewater probes, mini-wells, diffusion samplers, seepage meters, and in situ chambers.

A matrix was developed to evaluate these technologies. The factors for consideration of each technology include technical performance/applicability, developmental status, reliability, and cost. A panel of experts will fill out the matrix and the selected technologies will then be evaluated for a demonstration based on the panel results.

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1 Introduction

The U.S. Navy is identifying, assessing, and remediating a large number of terrestrial hazardous waste sites. Many sites are located adjacent to harbors, bays, estuaries, wetlands, and other coastal environments. Approximately one-third of all U.S. Navy landfills have groundwater infiltrating the waste, and as a result the Navy must determine if contaminants from these sites are migrating into marine systems at levels that pose a threat to the environment.

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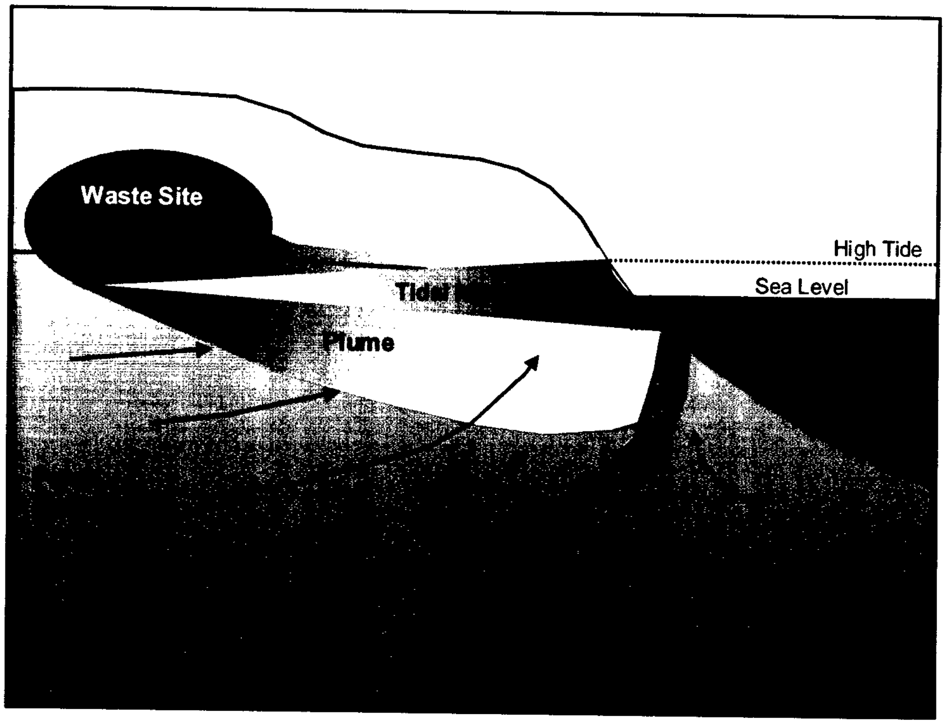

Figure 1. Conceptual representation of the coastal contaminant migration process and associated groundwater–surface water interaction.

2 Regulations

Coastal and Landfill Regulations

Many laws may govern a coastal waste site. The first comprehensive federal effort to deal with the solid-waste problem in general, and specifically hazardous waste, came with the Resource Conservation and Recovery Act (RCRA) of 1976. This act regulates anyone engaged in the creation, transportation, treatment, storage, and disposal of hazardous wastes (RCRA Subtitle C) and regulates the facilities for disposal of solid wastes (RCRA Subtitle D). However, many waste disposal sites were created before the passage of RCRA. The cleanup of these past waste disposal sites is principally regulated under the Comprehensive Response Compensation and Liability Act (CERCLA). In addition to these regulations, other regulations can be applied to a waste disposal site. These regulations include the National Environmental Policy Act: the Clean Water Act; the Safe Drinking Water Act; the Toxic Substances Control Act; the Clean Air Act; the Marine Protection, Research and Sanctuaries Act; the Coastal Zone Management and Improvement Act; the Fish and Wildlife Act; the Migratory Bird Treaty Act; the Rivers and Harbors Act; and the Endangered Species Act. Each measure, discussed in detail below, may be applicable to a coastal waste site.

National Environmental Policy Act

The National Environmental Policy Act (NEPA) ensures that environmental impacts are considered before the final decision-making process. The law requires that environmental impact statements be prepared for major actions. Specifically, 42 U.S.C. 4332 et seq states that "All agencies of the Federal Government shall - (c) include in every recommendation or report on proposals for legislation and other major Federal actions significantly affecting the quality of the human environment, a detailed statement by the responsible official on - (i) the environmental impact of the proposed action."

The statements must address the environmental impact of the proposed action, address any unavoidable environmental effects of the proposed actions, and consider alternatives to the proposed actions.

Clean Water Act

The Clean Water Act (CWA) limits pollutant discharges from point sources. The Environmental Protection Agency (EPA), or States with approved programs, issue pollution permits, known as National Pollution Discharge Elimination System (NPDES) permits. The CWA sets levels of technology that must be used to control various types of effluent; these limits must be incorporated into NPDES permits. EPA also promulgates nationwide effluent limitations for toxics and certain categories of new sources. NPDES permits must incorporate effluent limitations stringent enough to meet water-quality standards. States establish water-quality standards based on desired uses of the

particular water area. The CWA regulation of non-point source pollution is still in its infancy. States are developing and submitting for EPA approval non-point source pollution control plans.

Safe Drinking Water Act

The Safe Drinking Water Act (SDWA) protects the nation's drinking water supplies. The SDWA establishes national primary drinking water standards for public drinking water supplies for 83 contaminants. These standards are called maximum contaminant level standards, and each State enforces the standards.

Toxic Substances Control Act

The Toxic Substances Control Act (TSCA) allows EPA to require toxicity testing of chemicals if their effects are unknown. EPA can also prohibit the manufacture, sale, use, or disposal of a chemical if the compound represents an unreasonable risk to the environment or health. This act does not regulate pesticides, drugs, and nuclear materials.

Clean Air Act

The Clean Air Act provides clean air to protect human health. The act is composed of many parts, but the two parts most relevant to landfills are the ambient air-quality standards and the emission standards. The ambient air-quality standards set levels for criteria pollutants that are not to be exceeded. If they are exceeded, the State or area must develop a plan to bring the area into compliance with the law. The Clean Air Act has also established emission standards for various compounds from a particular type of source. If emissions from the source are above the standard, emissions must be controlled and reduced to levels below that set by the standard.

Marine Protection, Research, and Sanctuaries Act

The Marine Protection, Research, and Sanctuaries Act regulates ocean dumping. The act also establishes marine sanctuaries.

Coastal Zone Management and Improvement Act

The Coastal Zone Management and Improvement Act encourages States to manage and conserve coastal areas as a unique, irreplaceable resource. The act requires each State with a coastal zone management program to address pollution of coastal waters and to encourage each coastal State to improve coastal wetlands protection, natural hazards management, public beach access, marine debris management, assessments of coastal growth and development, and environmentally sound citing of coastal energy facilities.

Fish and Wildlife Act

The Fish and Wildlife Act established the Fish and Wildlife Service (FWS) and authorized the Secretary of the Interior to develop, advance, manage,

conserve, and protect fish and wildlife resources. Such authority can be used to protect areas vital to many fish and wildlife species.

Migratory Bird Treaty Act

The Migration Bird Treaty Act makes it unlawful at any time, by any means or in any manner to pursue, hunt, take, capture, kill, or attempt to take, capture, or kill any migratory bird, or any part, nest, or egg of any such bird administered by FWS, unless permitted.

Rivers and Harbors Act

The Rivers and Harbors Act requires that permits be obtained from the Army Corps of Engineers for dredge, fill, and other activities that could obstruct navigable waterways.

Endangered Species Act

The Endangered Species Act conserves endangered and threatened plants, animals, and their habitats. This act prohibits any federal agency from undertaking or funding a project that will threaten a rare or endangered species. The act can be used to restrict development or alterations of an area that is critical to a species.

Groundwater Monitoring Regulations and Requirements

Groundwater from a coastal waste site may require monitoring. A summary of the groundwater monitoring requirements for a landfill shows that monitoring a coastal site can be extensive. The Federal regulation references that govern monitoring for a landfill are as follows:

RCRA Regulations: 40 CFR, Subtitle C, Parts 264 and 265, Subpart F
RCRA Regulations: 40 CFR, Subtitle D, Part 258, Subpart E
CERCLA Regulations: 40 CFR, Part 300
TSCA Regulations: 40 CFR, Part 702
RCRA Groundwater Monitoring Technical Enforcement Guidance Document
RCRA Groundwater Monitoring Systems

Each regulatory program has the same basic groundwater monitoring components; however, they may differ somewhat in monitoring frequencies and periods, required constituents for analysis, and unique State requirements or regulations.

With limited exceptions as stated in the various regulations, all owners and operators (O/Os) of hazardous and solid-waste facilities (including containers, tanks, surface impoundments, waste piles, land-treatment facilities, landfills, and incinerators) must implement and conduct a monitoring and response program. The groundwater-monitoring program must include a sampling and analysis plan that detects contaminants in the groundwater above background conditions. When hazardous constituents are detected in the groundwater at

the facility, the O/O must implement a compliance or assessment-monitoring program. Whenever a groundwater protection standard is exceeded, the O/O must implement a corrective action program.

The following sections provide a brief summary of the basic requirements for a site characterization and groundwater-monitoring program.

Site Characterization

The adequacy of an O/O's groundwater monitoring program hinges on the quality and quantity of the hydrogeologic data used in designing the program. Two basic objectives must be met before the site is considered to be adequately characterized: (1) Collect enough hydrogeologic information to adequately characterize, at a minimum, the uppermost aquifer at the site, including the identification of potential contaminant migration pathways, and the groundwater flow path and flow rates, and (2) use appropriate data collection, sampling, and analysis techniques in obtaining the hydrogeologic data to support of the design of the groundwater monitoring program. Site-specific factors must be considered at each location.

Various investigative techniques are available that all O/O's should use to characterize their sites. Initially, all available literature regarding the hydrogeology of the site should be reviewed before conducting a site-specific investigation. The following list of hydrogeologic investigative techniques may be used to characterize a site:

- Survey existing geologic information/aerial photographs
- Install soil borings/rock corings
- Perform material tests/grain size analyses and/or standard penetration tests
- Perform geophysical well logging (resistivity, electromagnetic conductance, gamma, etc.)
- Perform permeability and/or hydraulic conductivity measurements of soil samples/cores
- Perform soil gas/geoprobe/hydropunch surveys
- Install groundwater monitoring wells/piezometers at different aquifer depths/locations
- Perform slug and/or pumping tests at monitoring wells
- Consider tracer studies and other methods to determine lateral and vertical migration pathways

Using these investigative techniques, the following data presentations and assessment outputs should be created:

- Narrative description of the hydrogeology of the site
- Geologic cross-sections
- Soil boring/coring logs

- Structure contour maps of the aquifer and/or confining layers
- Raw data and analysis of geophysical investigations
- Raw data and analysis of material testing
- Groundwater well completion logs
- Narrative description of the groundwater flow and migration characteristics
- Groundwater table potentiometric surface map
- Raw data and analysis of tracer studies and slug and/or pump tests

The soil boring/well installation program should be adequate to characterize the site and to determine the potential contaminant migration pathways. Initial boreholes should be installed at a density that provides information to determine the presence and migration of contaminants. Initial boreholes should be drilled into the first confining layer beneath the uppermost aquifer. Boreholes should be placed at strategic locations to adequately characterize the site and may be located based on indirect or geophysical techniques. Initially, continuous coring should be performed at the site to characterize the geology. Sufficient laboratory analyses and material testing should be performed to verify the field determination of the geologic logging.

Groundwater Detection Monitoring

Placement and screening of groundwater wells at a site is based on the result of a thorough site characterization investigation. This information (geologic strata, groundwater flow direction, gradient, velocities, etc.) is the foundation for the entire groundwater-monitoring program. Up-gradient well(s) must be located in a position where background water-quality conditions in the uppermost aquifer can be detected, and are unaffected by any potential site contaminants. A sufficient number of down-gradient monitoring wells (usually a minimum of three) will detect any potential contaminant release from the regulated unit (i.e., landfill).

It is important to remember that potential contaminant pathways are three-dimensional (3-D), and detection monitoring wells may be required at different depths in the uppermost aquifer and sometimes in lower aquifers. The horizontal and vertical (screened intervals) placement of the detection monitoring wells depends on site hydrogeologic conditions. The wells should typically be placed immediately adjacent to the hazardous waste management unit (i.e., landfill) and predicated on the ability to intercept contaminant migration. Another factor in determining the location and depth of the monitoring wells is the physical and chemical characteristics of the hazardous waste constituents (i.e., dispersion, solubility, non-aqueous phased liquids, etc.).

When designing and constructing groundwater monitoring wells, factors such as drilling methods, well construction materials, filter packs, sealant materials,

well intakes (screen/perforation sizes, depth intervals, and lengths), well development, and appropriate documentation should be considered.

A written sampling and analysis plan should include procedures and techniques for groundwater sample collection, sample preservation, field and laboratory quality assurance/quality control (QA/QC) procedures, sample shipment and analytical procedures, and chain-of-custody control.

Once the analytical data from the laboratory have been validated, a statistical analysis should be performed on the data to determine if the constituents from the hazardous waste management unit have potentially or significantly affected the groundwater quality.

Groundwater Assessment or Compliance Monitoring

Once contaminant leakage has been detected as a result of the groundwater-monitoring program, the O/O must undertake a more aggressive groundwater-monitoring program. The O/O must also establish the rate and extent of contaminant migration. This information is needed to evaluate the need for any corrective action requirements.

Assuming the contamination is not the result of false positives, a site that has detected statistically significant groundwater contamination requires a written assessment-monitoring plan. Any combination of additional monitoring wells, additional analytical constituents, or an increased frequency of monitoring may be required. The assessment plan should describe any potential migration pathways and implement a plan to fully characterize the rate and extent of contamination. A combination of direct methods (installing additional groundwater wells) and indirect methods (groundwater fate and transport or mathematical modeling) may be used to predict the extent of contamination. Additional site characterization may also be required.

Once the additional assessment or compliance monitoring data have been collected and evaluated, it should be determined if any groundwater protection standards have been exceeded and if a site requires a corrective action program.

3 Site Summaries

This section provides information about sites that have groundwater migration issues.

Summary of Landfills with Tidal Influence

Table 1 is a summary of the results found at the various Engineering Field Activities and Engineering Field Divisions from the initial decision report on coastal landfill remediation–subsurface barriers. Approximately one-third of the 465 landfill sites have groundwater contamination and groundwater infiltrating the waste, and it is estimated that one-fifth of the landfills have a tidal influence.

Descriptions of sites with groundwater migration issues are included to illustrate these issues. These sites are spread throughout the country, from the East Coast to Hawaii.

Table 1. Navy landfill summary.

EFA/EFD	Groundwater Contamination	Tidal Infiltration	Groundwater Infiltration
Atlantic Division	29	14	16
EFA Chesapeake	14	4	10
Northern Division	20	10	18
EFA West	29	14	31
South West Division	19	15	13
EFA Midwest	3	0	3
EFA North West	6	8	10
Pacific Division	5	10	8
Southern Division	27	26	50
TOTALS	152	101	159

Naval Fuel Depot Point Molate

Site 3 Treatment Pond Area. Site 3 (Figure 2) is located on a flat, filled area adjacent to the San Francisco Bay and is approximately the size of a football field. The site consists of three stormwater treatment ponds (300 to 400 feet long), a stormwater treatment plant, a groundwater containment wall and extraction trench, a groundwater treatment plant, and a domestic sewage treatment plant, all constructed over a former sump pond. Weathered diesel and heavier, tar-like, number 6 bunker fuel exist throughout the site. Free product varies from 0 to 3.6 feet.

In 1995, the Water Board required the installation of a 25-foot-deep sheet pile containment wall, 10 to 20 feet from the San Francisco Bay shoreline. Four extraction wells pump free product and water into an extraction system; the water is treated and then discharged to the Bay.

The stormwater treatment plant captures stormwater runoff from the fuel storage tanks and catch basins. The stormwater first passes through an oil/water separator and then to the three treatment ponds that are above ground bioreactors. After 2 to 4 weeks, the stormwater is pumped through a treatment plant that consists of sand filtration and granular-activated carbon before it is discharged to San Francisco Bay.

Site 4 Shoreline Perimeter. Site 4 (Figure 2) includes the entire perimeter along San Francisco Bay. This site was included as an Installation Restoration site because of concerns over historical fuel spills and leaks, which may have impacted bay waters and sediment. Investigations at Site 4 included soil and groundwater sampling along the shoreline.

Site 4 soil samples were collected during the site investigation and the shoreline investigation. Chemical analytical results indicated total petroleum hydrocarbons (TPHs), benzene-toluene-ethylene-xylene (BTEX), and polycyclic aromatic hydrocarbons (PAHs).

Groundwater samples were collected from shoreline wells during the four quarterly groundwater-sampling events in 1994. TPH, BTEX, and chlorinated volatile organic carbons (VOCs) were the most commonly detected contaminants in Site 4 groundwater. Detections in groundwater samples consistently included contaminants. Free product has also been identified in wells within Site 4.

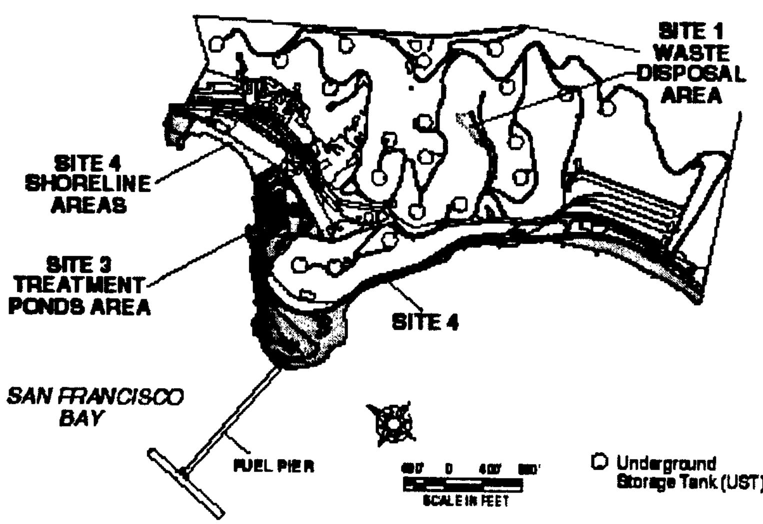

Figure 2. Site map of Naval Fuel Depot Point Molate.

Naval Station Treasure Island

Base-wide areas are impacted by diesel and gasoline from fuel lines, Underground Storage Tanks (USTs), and TPH plumes (Figure 3). Investigation of the fuel lines proceeded by using screening levels previously developed from bioassay data for aquatic receptors. At Naval Station (NS) Treasure Island, a tiered approach was used to evaluate TPH-affected areas. Based on facility-specific bioassay results and modifications proposed by the Regional Water Quality Control Board (RWQCB), TPH concentrations below 1.4 mg·L^{-1} in groundwater and 447 mg·kg^{-1} in soil have been determined to be protective of aquatic receptors (it is noted that exposure of aquatic receptors is the principal pathway of concern at Treasure Island). These values are used as first tier TPH screening levels. TPH concentrations exceeding the first tier screening levels were subsequently evaluated using TPH constituent- and site-specific data (for example, fate and transport modeling) and examined as part of NS Treasure Island monitored natural attenuation program. TPH concentrations that are determined to still exceed the 1.4 mg·L^{-1} TPH criterion at the shoreline (the proposed NS Treasure Island point of compliance) are then evaluated for cleanup. This NS Treasure Island TPH approach parallels the tiered protocol being developed by the Navy TPH working group and has been ongoing.

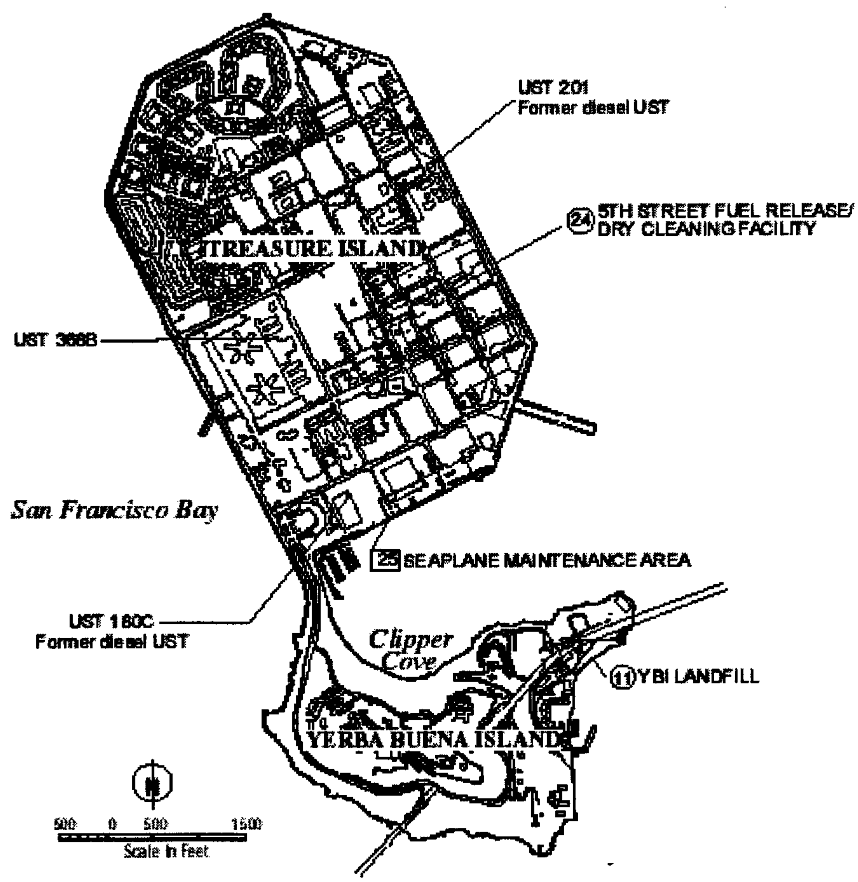

Figure 3. Site map of Naval Station Treasure Island.

The U.S. Navy uses modeling to evaluate whether TPH constituents will reach the shoreline. Previous modeling at one site, with conservative parameters, indicated TPH constituents (such as BTEX) would reach the shoreline at concentrations in excess of corresponding EPA ambient water-quality criteria.

Site 24 (5th Street Fuel Releases) exists because of a fuel line spill and sumps leading directly to the soil from a former dry-cleaning facility (Figure 3). By 1960, operation at the dry-cleaning facility had stopped, but current groundwater measurements still show solvents. A very conservative groundwater model shows that chlorinated solvents will reach the shoreline at a concentration that will exceed ambient water-quality criteria.

Naval Air Station North Island

Site 9, Chemical Waste Disposal Area. This site is a 38-acre parcel that operated as a waste disposal area from the 1940s to the late 1970s, before the Industrial Waste Treatment Plant (Site 11) began operation (Figure 4). It consisted of three major waste disposal operations: a shallow pit used for disposal of liquid wastes from portable tanks; four parallel trenches, each containing different types of wastes (solvents, caustics, acids, and semisynthetics consisting of ceramic and metallic compounds); a low-level radioactive material storage yard; and a large unimproved area used for burying drums containing unidentified wastes.

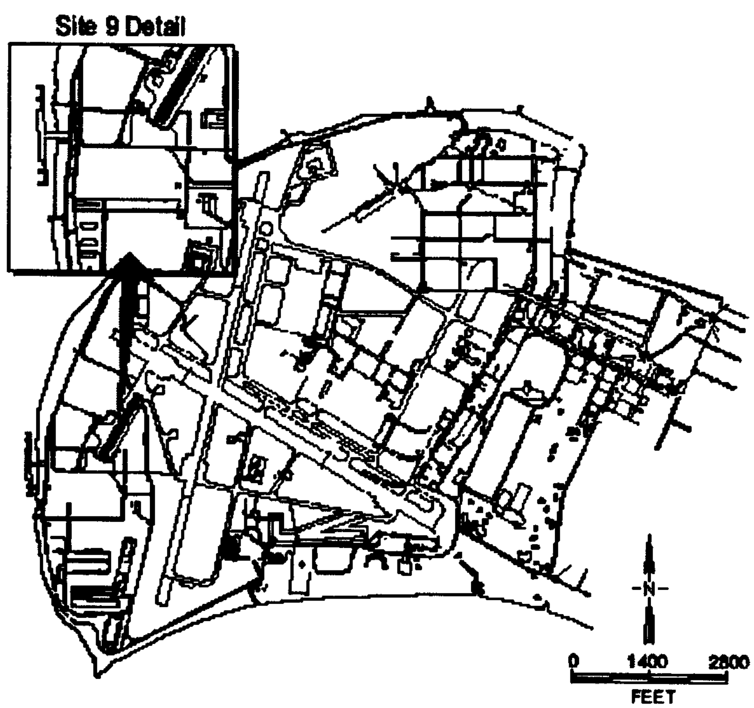

Figure 4. Naval Air Station North Island Site 9.

Previous modeling and measurements indicate VOCs are migrating into San Diego Bay from groundwater sources originating at Site 9. Groundwater modeling indicates that groundwater flow is directed from Site 9 toward the bay, and elevated concentrations of chlorinated solvents have been identified in sampling wells located along the western shore of North Island.

Several demonstrations of innovative cleanup technologies are also operating at Site 9. Space and Naval Warfare (SPAWAR) Systems Center, San Diego (SSC San Diego) has performed measurements with porewater probes and seepage meters to determine high flux areas.

Naval Base Ventura County NAS Point Mugu Site 1 - Lagoon Landfill

This site was a 25-acre landfill, trash-burning area, and dredge spoil storage area since 1952 (Figure 5). The landfill is no longer used and was closed in 1978. The eastern boundary of the landfill, adjacent to a lagoon, was partially contained by a berm composed of rubble and dredged material. However, this material was subject to erosion by tides and flooding of Calleguas Creek.

The Remedial Investigation phase that was performed at the site during Fiscal Year 1996 indicated the immediate need to perform a time-critical removal action (TCRA) to reduce the erosion. The decision was made to perform the TCRA. During the removal action, approximately 7 acres of the site were graded and capped with a chip seal surface. This surface is used as a laydown

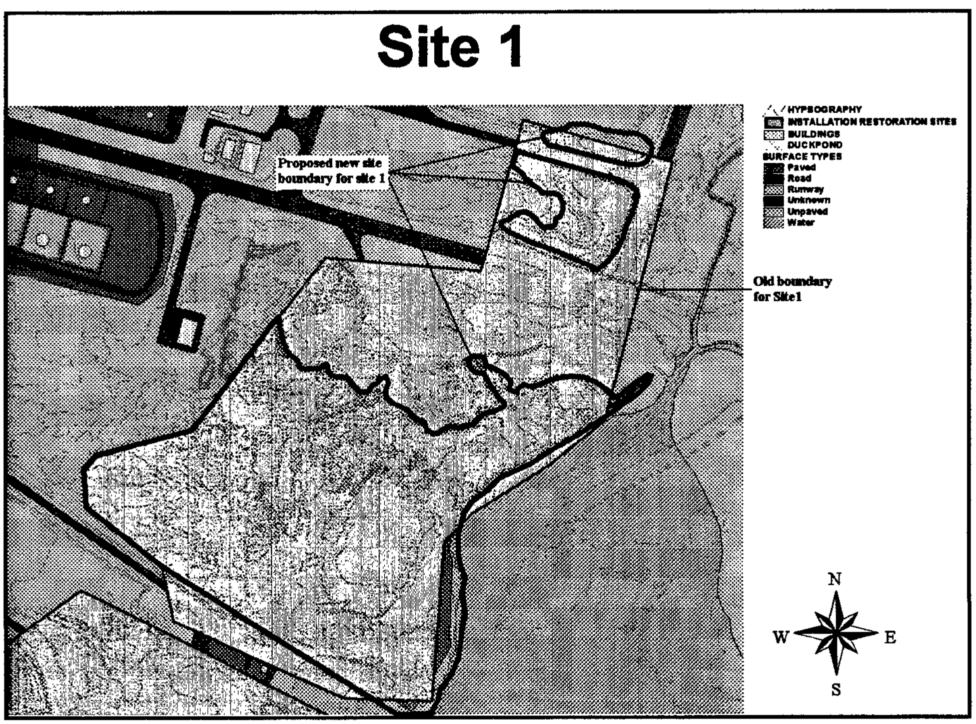

Figure 5. Naval Air Station Point Mugu Installation Restoration Site 1.

area. A rip-rap wall was also constructed to reduce further erosion of the shoreline and transport landfill materials into the lagoon.

A base-wide groundwater study was funded to address any concerns with the migration of contaminants from terrestrial sites on NAS Point Mugu to the lagoon, ocean, or lower aquifers. New monitoring wells were installed, quarterly groundwater data were collected, and tidal influence was studied. This information was used to perform modeling of Site 1 to determine any impacts to the lagoon.

Portsmouth Naval Shipyard

The 25-acre Jamaica Island Landfill (JILF) was used for hazardous and non-hazardous waste disposal from 1945 to 1978 (Figure 6). The landfill was created by filling tidal flats between the original Seavey's and Jamaica Islands from north to south, and forms the north and west shore of Clark Cove. According to archive records, the tidal flats that were inundated with disposal material appear to have supported various estuarine habitats including shell-fishing beds, fringing marshes along the shores of Seavey and Jamaica Islands, a benthic invertebrate habitat, a rocky shoreline habitat, and possibly eelgrass beds in adjacent subtidal areas. The filling activities, which took place over several decades, completely covered the estuarine resources where the landfill now resides and altered the river currents around Jamaica Island. Remnants of the old habitat found during the JILF investigations included an 8- to 30-ft thick layer of organic-rich silt and clay underlying most of the landfill, and extensive beach and tidal flat deposits under the overburden (McLaren/Hart Environmental Engineering Corp., 1992). The direct disposal of materials into the tidal area would have resulted in significant releases of contaminants through surface runoff, windblown dust, and refuse being pushed directly into the river.

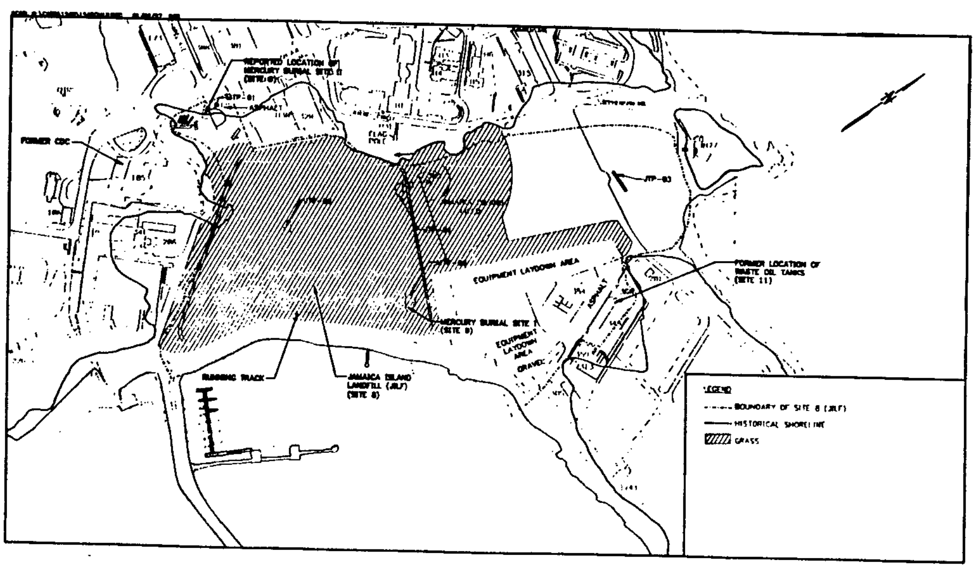

Figure 6. Portsmouth Naval Shipyard Jamaica Island Landfill Restoration Site 1.

Various materials, including sludges, solvents, asbestos, blasting grit, incinerator ash, and mercury-contaminated wastes contained within concrete vaults were disposed in the landfill. Waste oils containing polychlorinated biphenyls (PCBs) may also have been disposed in the landfill before 1972. In 1978, more than 82,571 cubic yards of sediments were dredged from Berths 6, 11, and 13 at the western end of the island and were disposed of over the landfill. This material was contained and capped by a clay barrier. Currently, the JILF is maintained as an open space and recreational area.

The presence of the marine silt and clay layer underlying the landfill could serve as a confining layer and would prevent the movement of contaminants due to the low porosity and high sorptive capacity of the clay material. Regional groundwater flow appears to be discharging upward from the bedrock, likely resulting in the flow being diverted "laterally beneath the clay layer toward the estuary" without coming into contact with the landfill material (McLaren/Hart Environmental Engineering Corp., 1992). Migration of landfill contaminants could be further hindered by the fill and cap materials used when the landfill was closed. However, there is evidence of tidal exchange and tidal influence on groundwater elevations near the southeastern edge of the landfill (along the shore of Clark Cove). Estuarine water has been detected in monitoring wells (McLaren/Hart Environmental Engineering Corp., 1992) and seepage samples (Johnston et al., 1994) taken along the edge of the landfill. Based on the available hydrogeological information, it is expected that most metals and organic compounds would be tightly sorbed to particles and would not readily migrate. This expectation is consistent with results of seepage sampling, which show that no organic contaminants have been detected (McLaren/Hart Environmental Engineering Corp., 1992; Johnston et al., 1994) and that most inorganic contaminants in the seep samples were below ambient water-quality criteria standards (Johnston et al., 1994). However, a "potential exists for inorganic contaminants to migrate via groundwater from JILF to [the] estuary...and...based on tidal influence... organic compounds may [also] be entering the estuary..." from the JILF (McLaren/Hart Environmental Engineering Corp., 1992).

Marine sediments collected along the face of JILF contained elevated concentrations of chromium, nickel, and lead. Algae *(Fucus vesiculosus)* samples were elevated in chromium, cadmium, lead, and nickel. Blue mussels *(Mytilus edulis)* had elevated levels of nickel, lead, and PCBs. Sediment and water sampling in Clark Cove conducted by McLaren/Hart Environmental Engineering Corp. during the Resource Conservation and Recovery Act facility investigation found no detectable levels of PCBs, pesticides, semivolatiles, or volatile compounds (except for unidentified aliphatic hydrocarbons and VOCS associated with laboratory solvents–acetone, chloroform, and carbon-tetrachioride). Measurements of TPH concentration ranged from 140 to 780 ppm, and metal including arsenic, chromium, copper, lead, mercury, and nickel

were detected at levels above the effects range-low (ER-L) toxicity threshold (McLaren/Hart Environmental Engineering Corp., 1992).

Pearl City Peninsula Landfill

The landfill occupies 67 acres of the Pearl City Peninsula, Oahu, Hawaii, and is bounded by the Waiawa Unit of the Pearl Harbor National Wildlife Refuge, the Middle Loch of Pearl Harbor, the inactive Pearl City Municipal Sewage Treatment Plant (STP), Waiawa Stream, and a 40-foot wide railway right-of-way, which is now used as a bicycle pathway (Figure 7). Authorized sanitary landfill operations began at the site in 1965, and the landfill was closed in 1976. The site is expected to remain closed with restricted public access.

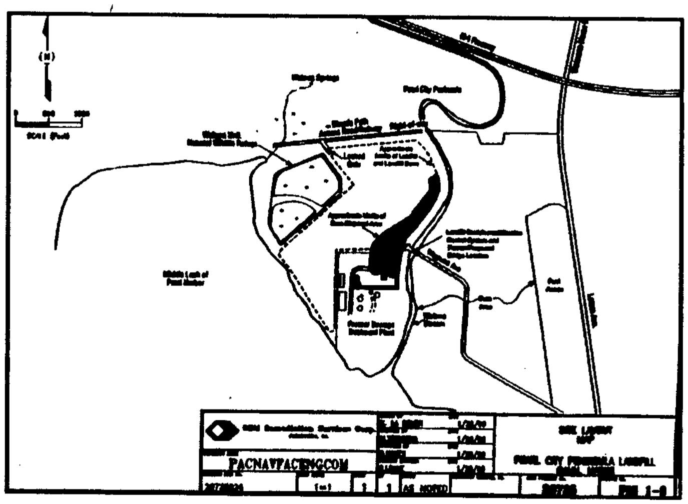

Figure 7. Pearl City Peninsula Landfill.

Although most of the landfill is surrounded by a perimeter berm, geotechnical and groundwater sampling results suggest that the berm is permeable. Landfill groundwater may therefore be discharged to Pearl Harbor, Waiawa Stream, or the Waiawa Unit (depending on weather conditions). Ecological risk assessment results indicate, however, that landfill groundwater contaminants are unlikely to threaten ecological receptors. Dilution due to tidal mixing in the harbor and surface water flow in Waiawa Stream and the Waiawa Unit greatly reduces groundwater contaminant concentrations upon discharge from the landfill aquifer.

A layer of basalt gravel ranging from 1 to 3 feet in thickness covers the landfill refuse. Sampling results indicate that the cover material is unlikely to threaten human or environmental receptors. The flux of landfill gas released through the cover is low, and risk assessment results suggest that landfill groundwater, which is not considered a potable water source, is unlikely to threaten human health or the environment; therefore, gas collection and leachate control are not necessary.

The Waiawa Unit is an intensely managed wetland that covers approximately 25 acres immediately northwest of the landfill. Two shallow ponds occupy most of the area. The ponds are supplied with fresh water from the Waiawa Spring Complex (located approximately 1000 feet to the north) and drain into Pearl Harbor. Ecological risk assessment results indicate that landfill groundwater is unlikely to threaten the ecological receptors that inhabit the Unit. Groundwater discharged from the landfill represents only a small fraction of the total volume of water flowing through the ponds. Contaminated surface and groundwater sources up-gradient of the landfill apparently contribute the bulk of the contamination load entering the ponds.

Elevated dioxin/furan, PCB, and arsenic concentrations were detected in surface and subsurface soil samples from an ash layer in the southeast corner of the landfill. The ash layer is apparently not restricted to U.S. Navy property; dioxins/furans have also been detected in soil on adjacent City and County of Honolulu-owned property occupied by an inactive STP. Human health risk assessment results indicate that direct exposure to ash and contaminated soil is the only mechanism likely to threaten human health. Ecological receptors in Waiawa Stream may be at risk due to the potential for surface runoff to erode and transport ash and contaminated soil to Waiawa Stream. The contaminants of concern are not readily leachable in soil due to their very low solubility and strong tendency to sorb to soil particles; therefore, surface water infiltration is a minor concern, and contaminant migration to groundwater is unlikely.

Investigations completed since landfill closure have not concluded that contaminants from the site are threatening human health and the environment. However, potential threats include direct exposure of humans to contaminated soils on-site and exposure of off-site ecological receptors to landfill-derived contaminants through direct contact with surface water and sediment.

The recommended option, Long-Term Monitoring Only, proposes a 5-year groundwater-monitoring program using 16 wells or piezometers along the landfill boundary. Landfill gas would be monitored in gas monitoring wells installed around the perimeter of the landfill. The program may be modified if sampling results indicate the need for a change in the monitoring schedule, duration, or parameters. The recommended option also proposes a 10-year monitoring program to detect future increases in the Waiawa Unit surface water and sediment toxicity or contaminant concentrations. The monitoring program may be suspended or discontinued if toxicity is not increasing or if the concentrations of contaminants known to occur in the landfill are not increasing in Waiawa Unit surface water or sediments. To better define baseline conditions within the Unit, additional ecological sampling would be implemented. Potential up-gradient or off-site contaminant sources would also be investigated to confirm that landfill contaminants are unlikely to threaten

the Waiawa Unit. The additional sampling programs would be developed in cooperation with concerned stakeholders.

4 Coastal Contaminant Migration Monitoring Technologies

Groundwater models are currently the method of choice for evaluating whether groundwater is impacting a coastal zone such as a bay or estuary. While this review focuses on measurement technologies, it is important to mention the role of models and their relationship to measurements and flow prediction.

Groundwater Models

Technology Description
Groundwater modeling is a computer-based method for mathematical analysis of the mechanisms and controls affecting groundwater systems (Van der Heijde, El-Kadi, and Williams, 1988). Analytical and numerical models are used extensively in simulating groundwater flow (Fetter, 1994), with applications ranging from one-dimensional, steady-state, flow prediction to 3-D, time-dependent flow, transport, and partitioning simulation (Van der Heijde, 1996). Models were developed for the hydrogeological processes of flow, transport, and transformation with many specific applications. These applications have increased enormously, parallel to the advancements in computer software technology. For example, models have been developed specifically for estimation of leachate generation at a waste facility, evaluation of various remedial activities, risk assessment, biodegradation, waste classification, etc. Models are often used in an integrated approach with measurements. Model loading terms, initial conditions, boundary conditions, calibration, and validation may all require measurement data.

Developmental Status
Many different types of models are available to simulate different groundwater systems, depending on the purpose of the study. Model selection generally depends on the complexity of the groundwater system. If the system is in steady-state condition during simulation, a simple analytical model may be sufficient to simulate a flow and transport. However, systems with transient conditions, heterogeneities, anisotropies, and multi-aquifer flow and transport can only be simulated accurately with numerical models.

Common numerical models include MODFLOW, GMS, VS2DT, 3DFEMFA, SEEP/W, and SUTRA. MODFLOW is a U.S. Geological Survey (USGS)-developed, modular, 3-D groundwater flow model used to simulate systems for water supply, containment, remediation, and mine dewatering. VS2DT is another USGS-developed program for flow and solute transport in variably saturated, single-phase flow in porous media. Simulated regions include one-dimensional columns, two-dimensional (2-D) vertical cross-sections, and axially symmetric, 3-D cylinders. The proprietary model, 3DFEMFAT (Scientific Software Group), is a 3-D finite-element model of flow and

transport through saturated–unsaturated media. Typical applications include infiltration, well-head protection, agriculture pesticides, sanitary landfill, radionuclide disposal sites, hazardous waste disposal sites, density-induced flow and transport, and saltwater intrusion. 3DFEMFAT supports simulations of flow only, transport only, combined sequential flow and transport, or coupled density-dependent flow and transport. SEEP/W is a proprietary finite-element software product (Geo-Slope International) that models seepage problems involving movement and porewater pressure distribution within porous materials such as soil and rock. SUTRA (developed by USGS) is a coupled groundwater flow and quality model. The model simulates energy and solute transport in saturated and unsaturated media and may also account for variability of density with temperature when simulating the heat transport.

Applications and Limitations

Groundwater models are practical, descriptive, and predictive problem-solving tools that assess the response of subsurface systems to variations in existing and potential environmental stresses. Groundwater models have various applications, including simulating and evaluating natural attenuation, optimizing groundwater remediation systems, designing pumping well capture zones, and studying watershed management. Where precise aquifer and contaminant characteristics have been reasonably well-established, groundwater models may also provide a viable method to predict contaminant fate and transport in complex subsurface systems.

Simulation of complex groundwater systems often requires the characterization of the hydrology, physical transport processes, geochemistry, contaminant chemistry, and biochemistry of the system, making groundwater modeling highly multidisciplinary (Van der Heijde and Elnawawy, 1993). Groundwater models also depend on several factors such as geology and parameters. Documentation for groundwater models can often be insufficient in determining the implementation of boundary conditions in the model. Most groundwater modeling software packages also address only a limited number of conditions that are actually encountered in the field (Van der Heijde, 1996). While groundwater models are only estimations used to describe complex systems, they can provide realistic, quantitative information for efficient resource use when additional field data collection is required and financial resources are limited.

The costs associated with groundwater modeling can be estimated from a recent contract task order (CTO) to assess groundwater migration. CTO 149 for NAS Point Mugu involved the installation of new monitoring wells, the collection of quarterly groundwater data, a tidal influence study, and the modeling of nine sites. The cost of this CTO was $1,850,952. The cost per site was $205,661. Other U.S. Navy bases have performed the same type of study, such as the Naval Construction Battalion Center (NCBC) Port Huenme, but their costs per site were even higher. Therefore, the cost of $205,661

represents a minimum number for the costs associated with groundwater modeling.

Flow Detection

The advective flow of groundwater to coastal water is called submarine groundwater discharge (SGWD) (Simmons et al., 1992). In freshwater systems, the exchange of water between surface waters and groundwater is generally referred to as hyporheic flow. A number of technologies exist or are under development to detect SGWD and hyporheic flow. These technologies range from the more quantitative detection methods such as seepage meters (Lee, 1977; Chadwick et al., 1999) and 3-D thermal gradient flow meters (Ballard, Barker, and Nichols, 1994) to indirect techniques such as piezometers (Lee and Cherry, 1978) and dye tracer injection (Turner Designs, 2000), and generalized detection techniques such as thermal plume mapping by infrared (IR) detection (Portnoy et al., 1998; Urish, 1999) and naturally occurring tracers. These techniques may be used together or in concert with analytical or numerical models. The following subsections describe each technology, its developmental status, applicability, and limitations.

Seepage Meters

Technology Description

Seepage meters were originally developed in the 1970s to assess SGWD in lakes and estuaries (Lee, 1977). The prototype instrument described by Lee (1977) consisted of a bottomless cylinder vented to a deflated plastic bag (Figure 8). The cylinder is implanted into the sediment, allowed to stabilize, and then the sampling bag is attached to the vent.

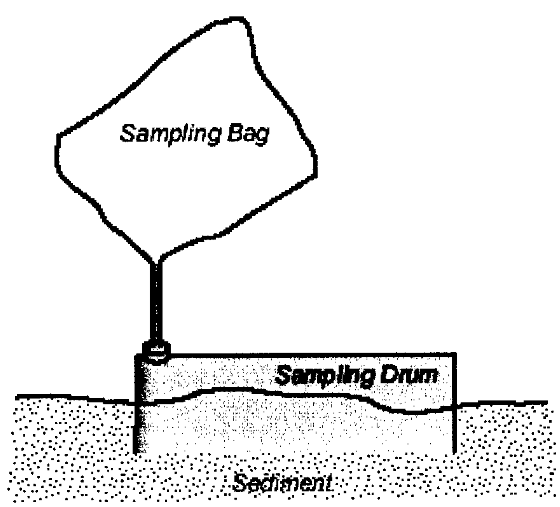

Figure 8. A traditional seepage meter showing typical placement in the sediment (adapted from Lee and Cherry, 1978).

Groundwater migrating across the interface is then channeled by the cylinder into the bag. The seepage velocity is determined by the equation, $v = A \cdot V/t$, where v is the seepage velocity, A is the area of sediment covered by the seepage meter, V is the net volume of water collected in the bag, and t is the elapsed time that the bag was in place. If the bag is pre-filled with water, then seepage from the surface water into the sediment can also be detected.

Developmental Status

Seepage meters continue to be refined and applied in various settings. Recent developments include adaptation for automated multiple sample collection (Chadwick et al., 1999), continuous flow detection using mechanical flow meters (Linke et al., 1994), thermistor flow meters (Linke et al., 1994), tracer injection (Tyron and Brown, 1999), and ultrasonic travel-time flow meters (Paulsen, Smith, and Wong, 1997). The following subsections describe each adaptation.

Multi-Sample Seepage Meter: Chadwick et al. (1999) describe a modified seepage meter system based on the standard seepage meter geometry used in previous studies. However, instead of a single sampling bag, a multi-port sampling configuration was used (Figure 9). The system incorporated two rotary selector valves that allowed six samples bags to be attached. A control system attached to the valves allowed sampling at pre-selected intervals. As a result, the meter can delineate variations in seepage over tidal cycles in coastal waters.

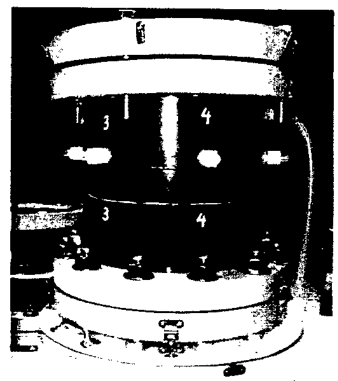

Figure 9. The multi-sample seepage meter showing the polyethylene drum (bottom) and multiport sampling module (top). Sampling bags connect to each of the six sampling ports on the meter.

Mechanical Flow Meter: Linke et al. (1994) describe a seepage meter with a mechanical flow meter in place of sampling bags. A Bernoulli-type mechanical flow meter was attached to the exhaust port on the top of the seepage drum and a camera recorded the flow reading. The calibrated flow meter provides a measurement range of about 0.01 to 4.0 ml min^{-1}. The meter requires careful calibration to compensate for fluid viscosity (as a function of temperature, salinity, and pressure), and for the back pressure induced by the small diameter of the exhaust port (3 mm^2).

Thermistor Flow Meter: Linke et al. (1994) also describe a thermistor (hot-bead) flow meter connected to a seepage meter. The thermistor flow meter measures flow rates from about 0.01 to 50 cm s^{-1}, and data can be recorded directly to a data logger.

Tracer Injection Flow Meter: Tryon and Brown (1999) present the design and initial results from a seepage meter equipped with a tracer-injection flow

meter. The water-and-geochemical flux meter (WGF-meter; Figure 10) measures fluid velocities through the sediment surface on the order of 0.1 to 100 mm y^{-1}. The WGF-meter is similar to traditional seepage meters; it channels groundwater flow at the sediment–water interface through an inverted-drum type chamber. The technology differs significantly in the manner in which it detects the flux rate and chemical properties of the flow. The meter uses the dilution of a chemical tracer to measure flow through the chamber. The tracer solution is injected into the seepage meter exhaust stream by two osmotic pumps. The same pumps are then used to sample the vent fluid/tracer mixture from downstream of the tracer injection port. The seepage rate is then quantified by analysis of the tracer concentration in the sample volume. This method allows direct measurements at low flux-rate vents and regions of slow diffuse flow.

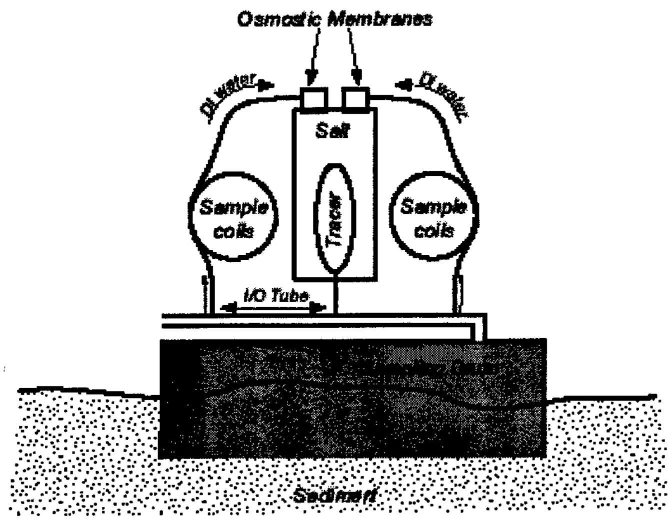

Figure 10. The WGF seepage meter showing schematically the tracer injection flow meter technique (adapted from Tryon and Brown, 1999.)

Ultrasonic Flow Meter: Paulsen et al. (1997) describe an ultrasonic flow meter that uses continuous flow monitoring (Figure 11). The flow from the sampling drum is led to a flow tube equipped with two ultrasonic piezoelectric transducers. As water passes through the ultrasonic beam path, the difference in travel times of the ultrasonic signals is directly proportional to the direction and velocity of the flow and can be used to determine the flow rate. The meter also detects reversals of flow such as a negative groundwater flux across an interface. In the field, the data logger and a backup battery are often housed in a buoy anchored to shore so that long-term, continuous measurements are made with a minimal risk of equipment damage. The battery life of the logger is approximately 12 hours, while the backup battery lasts approximately 48 hours.

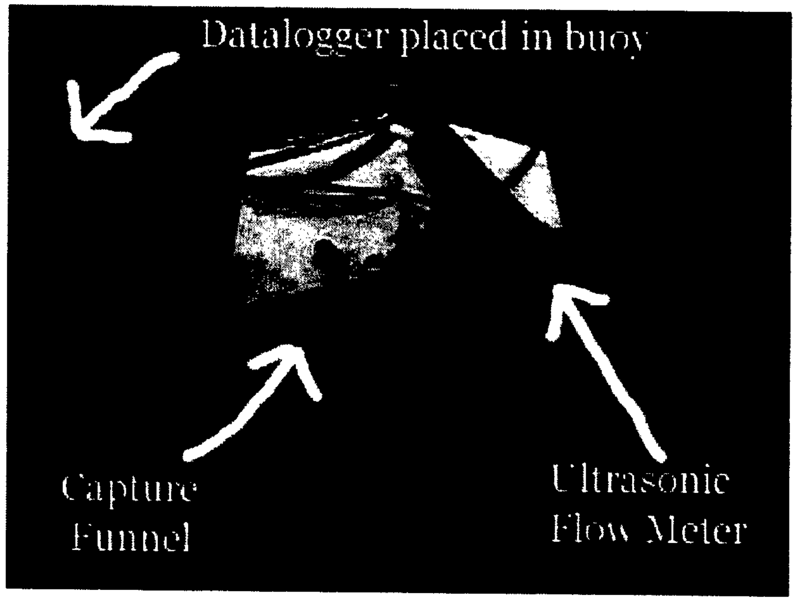

Figure 11. Seepage meter with ultrasonic flow detection.

Applications and Limitations
Seepage meters detect groundwater flow in a wide variety of settings including lakes and streams (Lee, 1977; Lock and John, 1978; Brock et al., 1982; Belanger and Mikutel, 1985; Cherkauer and McBride, 1988; Shaw et al., 1990), estuaries and bays (Lee, 1977; Bokuniewicz, 1980; Zimmerman, Montgomery, and Carlson, 1985; Simmons et al., 1991; Simmons et al., 1992), coral reefs (D'Elia, Web, and Porter, 1981; Lewis, 1987; Simmons and Netherton, 1986), and continental shelf waters (Simmons et al., 1992; Linke et al., 1994).

Traditional seepage meters are limited in detecting small seepage rates. They are also subject to errors associated with flow-field deflection, frictional resistance, head loss, and anomalous short-term influx when sampling bags are not pre-filled (Belanger and Montgomery, 1992; Shaw and Prepas, 1989). As described above, many limitations may be overcome by using improved sampling and flow measurement techniques.

Thermal Gradient Flow Meters

Technology Description
Heat-pulse groundwater flow meters have been used to measure groundwater flow in monitoring wells (Kerfoot and Massard, 1985). These meters heat the groundwater in a pulsed mode and then detect the 2-D horizontal flow components by measuring the thermal bias created as water flows through the meter. The linear relationship between the thermal conductance bias and flow rate determine the velocity (Kerfoot, 1982). Ballard et al. (1994) describe the In Situ Permeable Flow Sensor, a similar technique for direct, in situ measurement of groundwater flow (Figure 12). In this method, the probe is installed

directly into the saturated soil media (not a well) and a thermal perturbation technique detects flow. The meter uses a resistance heater to heat a groundwater volume of ~1 m^3 around the probe. An array of 30 thermistors located beneath the skin of the probe detects small-scale perturbations in the temperature distribution that arise from the flow of groundwater past the device. This technique provides magnitude and direction of groundwater flow in three dimensions, with theoretical detection as low as ~1 $m \cdot yr^{-1}$.

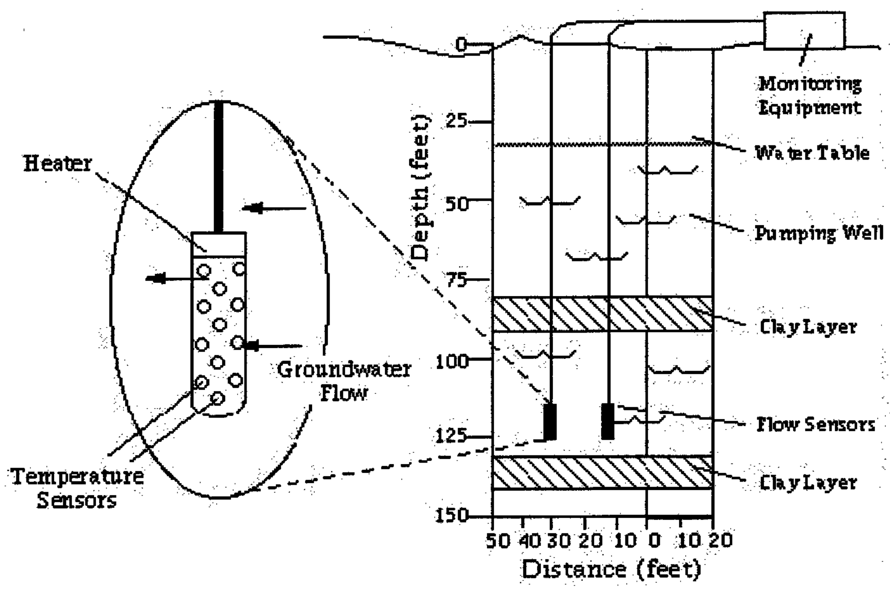

Figure 12. A schematic view of the In Situ Permeable Flow Sensor (from U.S. Department of Energy, 1995).

Developmental Status

Thermal flow probes have been demonstrated at a number of terrestrial sites. Recent publications indicate that further testing is still required, but initial test results appear promising (Ballard, 1996; Ballard et al., 1994).

Applications and Limitations

Thermal flow probes may have application in a wide variety of groundwater flow detection studies; however, the number of groundwater–surface water interaction applications attempted appears limited. The probes have advantages over traditional hydraulic gradient measurements because they can measure either 2-D or 3-D flow from a single installation, eliminate the need for additional slug/pump testing for hydraulic conductivity, and provide point measurements as opposed to average flow estimates over large areas. Thermal flow probes that are installed directly into the saturated soil avoid problems associated with screening effects on flow measurements observed in well-type probes. The probes can be left in place for up to about 1 year. Some drawbacks of the In Situ Permeable Flow Sensors are that they generally cannot be

removed once installed (at a cost of about $2500/probe) and convection associated with heating the water may affect flow.

Piezometers

Technology Description

A piezometer is a small-diameter well with a short-screened section at its end that measures the hydraulic head in an aquifer. In the field, a polyvinyl chloride (PVC) or stainless steel tube is typically used with evenly spaced small holes at the bottom of the tube to allow free-flowing groundwater to enter. Piezometers are placed at different depths to measure flow (Barnard and McBain, 1994). At least two piezometers must be used to determine the groundwater flow. According to Darcy's Law, the rate of water flow through a bed of specified strata is proportional to the difference of the heights of water between two piezometers and inversely proportional to the lengths of the flow path between piezometers (Fetter, 1994). In the field, the difference in pressure is measured by the difference of the water elevations in the tubes. These measurements may be done with an electric interface measuring tape, pressure transducer, or other methods.

Developmental Status

Piezometric methods for measuring hydraulic head are well developed. Recent developments indicate that substrate permeability can also be estimated with piezometers (Barnard and McBain, 1994). Drive-point piezometers for direct-push applications have become popular for water-level and water-quality monitoring (Cherry et al., 1993). For applications to groundwater–surface water interaction, miniature piezometers have been described for use directly in shallow coastal water for determining hydraulic head relative to surface water levels (Lee and Cherry, 1978; Winter, LaBaugh, and Rosenberry, 1988; Simmons et al., 1992).

Applications and Limitations

Piezometers have been used to evaluate water groundwater–surface water interactions in lakes and streams. If several piezometers are placed at different depths below the shoreline on the down-slope side of a lake, and they all have hydraulic heads higher than the elevation of a lake, a stagnation point is present, which means the lake will not leak from the bottom (Fetter, 1994). Piezometers are frequently used to evaluate the magnitude and landward extent of tidal influence on groundwater elevations in coastal regions (Ferdowsian and Ryder, 1997). Application is limited to sites where piezometers can be driven into the ground. Piezometers work best in unconsolidated deposits such as sands and gravels. This often proves problematic in developed coastal areas where shorelines have been stabilized with rip-rap or other impenetrable fill materials. Direct-push methods do not require a drill rig but will not work well in hard soil beds (Pitkin, Ingleton, and Cherry, 1994). Piezometers do not provide a direct measurement of

groundwater flow and rely on good estimates of lithology and hydraulic conductivity between the measurement points to allow accurate flow estimates.

Thermal Infrared Aerial Imagery

Technology Description
Thermal infrared aerial imagery has been used to detect groundwater discharge along shorelines of marshes and embayments in coastal New England (Portnoy et al., 1998). A super cooled detector mounted on a small aircraft measures the difference of thermal spectral response of the water along the coastline. Groundwater can be detected because it may sometimes be as much as 10 to 15° C colder than the surface water, especially in the summertime (Urish, 1999). If the groundwater is fresh, it will also have a lighter density than saltwater, making the temperature difference easier to detect because the freshwater tends to float above the saltwater.

Developmental Status
Thermal IR imagery is a well-developed technology that has been commercially available for many years. A number of platforms and detectors exist, ranging from hand-held to airborne to satellite-based systems. Using this technique to evaluate groundwater flow into surface waters is relatively new and has not been widely applied.

Applications and Limitations
This technology may find application in coastal sites with predominately good weather. The technique can only be used during good weather (cloud-free sky with very calm wind). Optimal time is immediately after sunset when the effect of direct solar effect is minimal and water temperature difference is still strong (Urish, 1999). Optimum time may also occur during low tide because the greatest discharge of groundwater often occurs at, or just after, low tide. In tests reviewed, two flight surveys were run about 1 hour apart to distinguish between fixed coastal features, which may also give a thermal response, and the moving plume of discharging freshwater. The method appears efficient and cost effective for detecting groundwater discharge under the proper circumstances. However, it is strictly qualitative and only indicates that discharge is occurring, but provides no information on flow magnitude. The number of published applications is also limited.

Tracer Injection

Technology Description
The tracer injection technique generally involves the introduction of an easily detectable constituent at one or more fixed points in the study area, and subsequent monitoring of the surrounding area to determine where the tracer migrates, and over what period of time. Common tracers include dyes

(Rhodamine WT, Fluorescein, Pontacyl brilliant-pink B) and dissolved salts (sodium bromide, sodium chloride, potassium chloride, lithium chloride) (Turner Designs, 2003; Goel, 1994; Replogle et al., 1976; Wright and Collins, 1964). The tracer is generally introduced via an existing monitoring well and may consist of a slug input or a continuous input for an extended period of time. Measurements of dye concentration are sampled at different wells downstream over a given period of time to predict the approximate subsurface flow of the groundwater (Kimball, 2000).

Developmental Status

While there have been a number of applications, the use of injected tracers in typical groundwater systems has not been thoroughly investigated (Turner Designs, 2003), particularly the effects of sorption of tracers on soil or subsurface strata.

Applications and Limitations

Tracer injection has been used in a variety of applications to groundwater flow detection including determination of flow path, flow velocity, travel time (residence time), water budget, hydraulic conductivity, dispersivity, and effective porosity (Cohen et al., 1994; Turner Designs, 2003). In applications to measurement of groundwater flow, adsorption of the tracer may confound results (Turner Designs, 2003). In a study of groundwater flow within a constructed fen, Goel (1994) found that sorption of Rhodamine WT on silty-loam material led to a retardation factor of about 7.2, indicating that the tracer movement would significantly underestimate the actual flow. In areas where the groundwater flow impinges on surface water, detection of the tracer may be difficult due to strong dilution, especially if the surface water is well-mixed by tidal, river, or wind-driven currents. In areas where groundwater flow is very slow, travel time measurements with tracers may require excessive time to achieve results, depending on the spatial separation of the injection and monitoring points. The appropriate tracer should be used based on their properties (toxicity, mobility, sorption) and the availability of reliable analytical techniques. The appropriate amount of tracer should be used based on background conditions, detection limit, and expected degree of tracer dilution (Cohen et al., 1994).

Colloidal Borescope

Technology Description

The colloidal borescope is an in situ observation system that determines groundwater flow velocity based on the movement of natural colloids in groundwater wells. The system consists of a charge-coupled device camera, an optical magnification lens, an illumination source, and a compass, all housed in a watertight stainless steel casing (Figure 12) (Kearl, 1997). The instrument transmits an electronic image to the surface through a cable and a special particle-tracking software program reads the borescope and analyzes

the images to calculate groundwater flow. The system is capable of measuring flow at selected depths within a well and has the ability to measure flow from individual fractures (Kearl et al., 1999). Flow direction and velocity in low- and high-permeability materials can be measured at velocities up to 3 $cm \cdot s^{-1}$ (Kearl and Roemer, 1998).

Developmental Status

The colloidal borescope (Figure 13) has been tested and demonstrated at many sites, including the Sandia Mountains in New Mexico (Kearl et al., 1999), the Department of Energy Kansas City Plant, the Portsmouth Gaseous Diffusion Plant, North Island Naval Air Station, Fallon Naval Air Station, the Fernald Plant, Hanford Reservation, the Savannah River Plant, Lawrence Livermore National Laboratory, and the Paducah Gaseous Diffusion Plant (Kearl and Roemer, 1998).

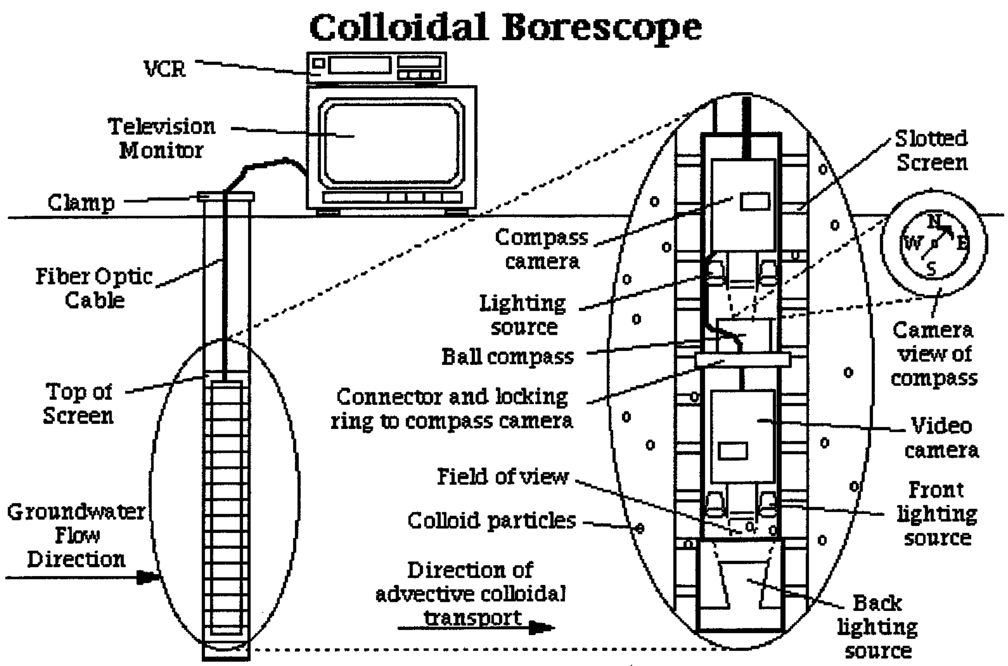

Figure 13. The colloidal borescope provides a direct means of determining groundwater flow direction and velocity. Reprinted from *Journal of Hydrology*, vol. 200, 1997, pp. 323–324, P. M. Kearl, "Observations of Particle Movement in a Monitoring Well Using the Colloidal Borescop," Copyright © 1997, with permission from Elsevier.

Applications and Limitations

The colloidal borescope system provides a direct measurement of ground-water flow direction and velocity. The technique is generally applicable to sites with existing monitoring wells or where wells can be installed. Current applications include the following:

- Site characterization by determining preferential flow paths and fractures

- Assessing heterogeneities associated with porous media

- Establishing the existence of immiscible contaminant layers and their associated flow properties

- Assessing the efficiency of groundwater remediation programs by determining the effective radius of influence of groundwater extraction systems

- Determining the amount of biological activity present in a bioremediation system

- Evaluating the effects of sampling on colloidal concentrations.

Potential applications include providing physical observation capabilities necessary to develop and confirm new, more accurate theoretical models of the porous media flow process and assessing the effects of water-sampling techniques on natural colloidal concentrations.

Borescope measurements are limited to horizontal flow (2-D) and may be hampered by vertical flow and/or well screen effects. Applications for the assessment of groundwater–surface water interaction appear limited. Additional work is underway to address variability observed in a well bore.

Natural Geochemical Tracers

Technology Description

Naturally occurring geochemical tracers represent a promising approach for regional scale assessment of groundwater–surface water interaction. Previous studies have used ^{222}Rn (Cable et al., 1996; Moore and Shaw, 1998; Hussain, Church, and Kim, 1998), ^{226}Ra (Moore, 1996; Moore and Shaw, 1998; Hussain et al., 1998), and barium (Moore and Shaw, 1998; Shaw et al., 1998) to estimate groundwater inflow rates (Figure 14). These tracers are favored because they are typically enriched in groundwater, often 3 to 4 orders of magnitude above coastal seawater. Nutrients and salinity have also been shown to be useful tracers in some areas (Moore and Shaw, 1998; Simmons et al., 1992). Most applications of natural tracers have been to evaluate the importance of submarine groundwater discharge in overall water or chemical budgets. The quantification of flow is generally based on measurement of surface water inventories of groundwater tracers and subsequent calculation of the groundwater discharge necessary to maintain the surface water budget.

Studies suggest that ^{226}Ra may be more useful for quantifying tidal pumping of groundwater due to its longer half-life, while ^{222}Rn may be more applicable as a tracer for groundwater discharge of freshwater (Hussain et al., 1998). Barium may be a good indicator of saline intrusion (Shaw et al., 1998).

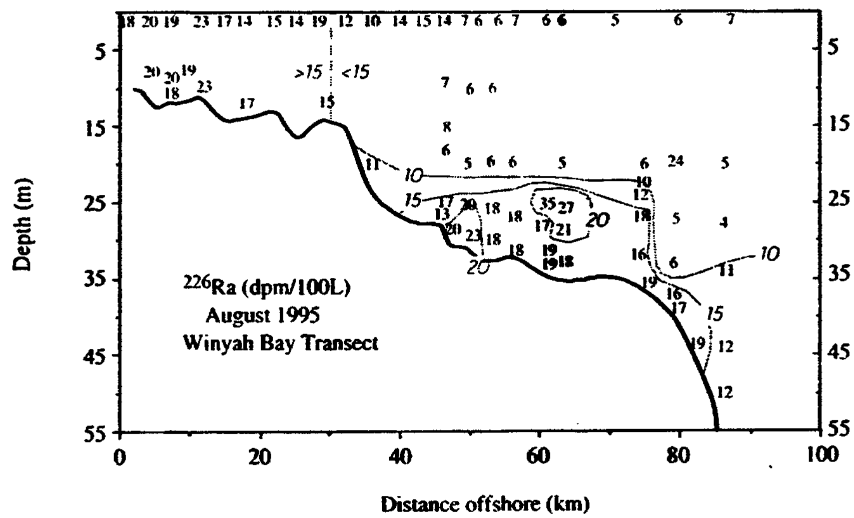

Figure 14. Offshore section of ^{226}Ra showing evidence of submarine groundwater discharge to the South Atlantic Bight. W. S. Moore and T. J. Shaw. "Chemical Signals from Submarine Fluid Advection onto the Continental Shelf," *Journal of Geophysical Research,* 103(C10), p. 21545, 1998. Published 1998, American Geophysical Union. Reproduced/modified by permission of American Geophysical Union.

Developmental Status

Natural tracers have gained acceptance as markers for groundwater–surface water interaction over the last 10 years based on a number of published studies. The methodologies, applications, and types of tracers continue to develop.

Applications and Limitations

Natural tracer techniques have application in coastal areas or bays near groundwater with a natural enrichment or deficit of the selected tracer. Examples include estimates of atmospheric and benthic exchange to San Francisco Bay (Hammond and Fuller, 1979), submarine spring discharge off the coast of Florida (Fanning et al., 1981), groundwater discharge to the South Atlantic Bight, groundwater discharge in the Gulf of Mexico (Cable et al., 1996), benthic exchange along the Southern California coast (Berelson, Hammond, and Fuller, 1982), and groundwater discharge in the Chesapeake Bay (Hussain et al., 1998).

Previous studies have primarily been limited to regional scale assessment based on overall water and chemical budgets. This approach has potential limitations in identifying source locations, and depends somewhat on

measuring or eliminating other tracer sources from the budget. Other possible tracer sources include diffusion from sediments, bioirrigation of sediments, and bubble ebullition. Many tracer techniques also depend on rather specialized isotope chemistry that may be unavailable.

Contaminant Detection

Pore Water Probes

Technology Description
The direct measurement of sediment pore water is generally done using one of four different methods: squeezing, centrifugation, vacuum filtration, and dialysis (Bufflap and Allen, 1995). The first two methods are considered ex situ techniques, requiring the extraction of sediments from their natural environment. These are the oldest and most widely used methods; however, the direct handling of sediment and porewater samples may lead to contamination and oxidation of the samples. The last two methods are considered in situ techniques. Because a sediment sample is not required, the potential for contamination is greatly decreased. Bufflap and Allen (1995) compared these four sampling methods and concluded that vacuum filtration had the best potential for producing artifact-free samples. However, this technique is limited at increased depths due to the high pressures that required extracting the samples.

Developmental Status
Several different techniques are used to extract sediment pore water. The type of techniques used generally depends on the type of environment in which a study occurs.

Squeezing Methods
Squeezing methods of pore water extraction either employ a means of pressurizing a section or an entire sediment core sample. This method usually uses gas pressure (Hartman, 1965; Lusczynski, 1961) or pistons that force pore water from the sample through an exit port (Lusczynski, 1961; Hartman, 1965; Jahnke, 1988). Jahnke (1988) describes an example of this method, where a simple porewater sampler was used that consisted of an acrylic core barrel with holes drilled at 1-, 2- and 3-cm spacings. The core barrel is inserted into a box core and pistons are placed at the top and bottom of the core barrel to pressurize the sample, forcing pore water out of the holes through 0.45-µm filters and into plastic syringes. This device is simple, fast, and cost-efficient, and is effective when in situ methods are not practical; however, handling of sediments may contribute to oxidation artifacts.

Centrifugation
Centrifugation is another ex situ method of extracting sediment pore water. Extracted samples are centrifuged to separate sediments from pore water. Batley and Giles (1979) have also used an inert fluorocarbon (FC-78) during

centrifugation to replace the pore water in the space between particles and force pore water to the surface. This method provides a greater percentage of pore water removal and alleviates the need for filtration of the extracted sample.

Vacuum Filtration

For in situ measurements, Watson and Frickers (1990) have developed a multilevel porewater sampler with a compact design that allows it to be deployed unattended in intertidal sediments, either inside benthic field chambers or aboard ship for porewater sampling in deeper cores. The unit is a solid acrylic cylinder with a series of five vertical holes drilled into the cylinder with their centers equally spaced around a 3.6-cm diameter circle, each fitted with a porous polyfluoro-tetraethylene (PFTE) insert. Pore water is extracted from each hole using a vacuum pump system. Watson and Frickers have also designed and tested a 10-hole unit, which they expect could easily be extended to 15 or 20 sampling intervals.

Chadwick et al. (1999) have developed an in situ collection method where pore water is extracted though a small-diameter, stainless steel probe using a syringe. Divers insert probes into the sediment and 100-mL samples are extracted and placed in pre-acidified vials for analysis.

Mini-Well

Mini-wells/mini-piezometers (Figure 15) can be installed permanently or temporarily and are very economical. Water levels are measured with a pressure manometer and samples are recovered using a peristaltic pump. Dean et al. (1999) developed a robust system of multilevel pore water sampling to investigate temporal and spatial effects of lake-aquifer interactions along an active beach face. Each array consists of a series of eight samplers made up of polyethylene tubing fitted with stainless steel screens. In situ pore water samples in the region of the sediment–water interface were extracted using a peristaltic pump to draw water from eight discreet depths. The arrays are inexpensive and easy to install; however, significant maintenance is required when they are used in a high-energy sampling site.

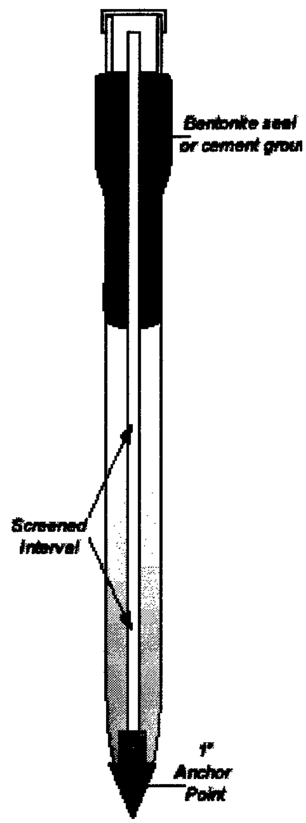

Figure 15. An example of a mini-piezometer/mini-well.

Dialysis

Dialysis is another in situ method for extracting pore water. Dialysis samplers, sometimes referred to as "peepers," usually consist of a sample chamber filled with distilled water and covered with a dialysis membrane that allows

chemical species to pass through the membrane until equilibrium with the ambient water is achieved (Carignan, 1984; Belzile and Tessier, 1990; DiToro et al., 1990). Dialysis samplers have also been developed that use a thin layer of ion exchange resin or gel (Davidson et al., 1991; Davidson and Zhang, 1994). Equilibrium times for thin-film resin and gel samplers are much shorter (< 1 hour) than for water-filled samplers (1 to 27 days).

Applications and Limitations

The analysis of sediment pore water has become increasingly important in determining and assessing sediment contamination and the contribution of sediment to the pollution of the overlying water column (Bufflap and Allen, 1995). Porewater samplers have applications in a wide range of environments, including intertidal sediments (Watson and Frickers, 1990), inside benthic field chambers (Watson and Frickers, 1990), and dynamic beach environments (Dean et al., 1999).

Sources of error that may alter trace metal concentrations in porewater samples are oxidation of anoxic pore waters, improper sediment sampling techniques, metal contamination, temperature artifacts, and lack of filtration (Bufflap and Allen, 1995).

Diffusion samplers

Technology Description

Several types of diffusion samplers are available for making in situ measurements of contaminants: vapor-diffusion samplers, water-to-water samplers, and diffusive gradients on thin films (DGTs). The vapor and water-to-water diffusion samplers consist of either air or deionized water, respectively, inside a polyethylene membrane. Each sampler is placed directly in the sediment and tied to a flag and a cable for easy retrieval (Lyford et al., 1999). These samplers are based on the ability of polyethylene to readily allow diffusion of VOCs such as aromatic petroleum hydrocarbons and chlorinated solvents while preventing the movement of water across the membrane. After sufficient equilibration time (≥ 14 days recommended), VOC concentrations of air or water in the sampler achieve equilibrium with VOC concentrations in the ambient water outside the sampler (Vroblesky, 1997). A field or laboratory gas chromatograph can then determine VOC concentrations in the contained air or water samples.

DGTs were designed in 1994 at Lancaster University to quantitatively measure in situ metal concentrations (ranging from ~ 0.1 ppb to 10 ppm) in sediment pore water (Windsor Scientific, Ltd., 2003; Davidson and Zhang, 1994). The probe is inserted directly into the sediment where trace metals are accumulated on a selective binding resin (sequestration layer) after passage through an open-pore gel (diffusive layer). As the DGT probe is continuously accumulating metal during deployment, the final measured mass is an integration of all metals in solution in contact with the device during the

deployment. The original probe developed by Davidson and Zhang (1994) used an acrylamide gel as a diffusion layer and Chelex as a sequestering plate. McCarthy et al. (1998) developed a similar device that uses a glass fiber filter for the diffusional layer, as this material does not adsorb either PAHs or dissolved organic matter (DOM).

The U.S. Geological Survey's Columbia Environmental Research Center recently developed a similar device, the Semi-Permeable Membrane Device (SPMD) (Figure 16). The SPMD was designed as a passive sampling technique for monitoring and assessing trace levels of organic compounds, including polychlorinated dioxin and furans, PAHs, PCBs, organochlorine insecticides, herbicides, and industrial chemicals. The SPMD is typically constructed from a layer of nonporous, low-density polyethylene that surrounds a sequestration medium. The sequestration medium generally consists of a thin film of large molecular weight lipid such as triolein, which mimics the absorption of contaminants into the fatty tissues of aquatic organisms (Figure 15) (Huckins et al., 1999).

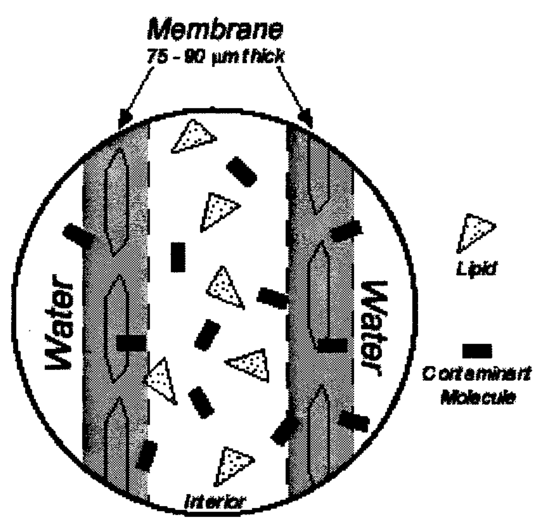

Figure 16. The Lipid-Containing Semi-Permeable Membrane Device (SPMD).

Developmental Status

Vapor-to-water and water-to-water diffusion sampling methods for determining groundwater concentrations of VOCs are relatively new. However, studies by Vroblesky (1997) and Vroblesky and Hyde (1997) suggest that this type of sampling method is a much more cost-efficient alternative to conventional purging and sampling.

DGTs and SPMDs are also very recent developments in measuring trace metal concentrations in sediment pore water. DGTs provide a much better spatial resolution than other technologies (i.e., dialysis peepers) and can be deployed

in large numbers because of relatively low cost and rapid equilibration time (Yu et al., 2000). The DGT probe also measures a much greater vertical resolution than other technologies by retaining vertical concentrations gradients in the pore water. SPMDs have primarily been used to measure contaminant concentrations in the water column; however, Huckins et al. (1999) and Axelman et al. (1999) imply that this device does have applications for measuring pore water contaminant concentrations.

Applications and Limitations

Diffusion samplers can be used to measure VOC concentrations in streambeds (Noonkester et al., 2000; Lyford et al., 1999; Vroblesky, 1997; Vroblesky and Hyde, 1997), wells (McClellan AFB/EM, 2000; Vroblesky, 1997; Vroblesky and Hyde, 1997), or other bodies of water where the samplers can be placed in an undisturbed area. A study by Vroblesky and Hyde (1997) shows similar concentrations obtained from diffusion samplers to those measured using traditional purging and sampling approaches (within ~12%). The lower cost of the diffusion sampling technique makes it a viable option for monitoring large well networks; however, the long equilibration period (≥ 14 days) must be considered when time is a factor. This method is also not applicable for measuring metals and other contaminants that do not readily diffuse across the semi-permeable membrane.

DGT probes have applications in a wide variety of aquatic environments, including rivers, lakes, estuaries, mudflats, and the deep sea. They have been interpreted to provide in situ information on labile metal species in seawater, remobilization fluxes, and concentration profiles at high resolution (1 mm) in freshwater, ultra-high resolution (100-μm) profiles in microbial mats, and remobilization fluxes in soils (McCarthy et al., 1998). The DGT probe is also not limited to measuring trace metals and can measure any component with a selective binding agent.

Seepage Meters

Technology Description

Seepage meters, previously described, have primarily been used to measure seepage rates of groundwater into aquatic environments. However, these instruments also have applications in measuring concentrations of various nutrients, gases, and contaminants in seepage water. Seepage meters consist of a cylinder with a large opening at the bottom and an exhaust port at the top that vents into a deflated plastic bag. The chamber is placed into the sediment to measure the rate of groundwater seepage across the sediment–water interface, based on the net volume of water collected in the bag. Samples from the collection bags are then analyzed for selected nutrient concentrations.

Developmental Status

Seepage meters have primarily been used to measure nutrient concentrations in groundwater seepage (Linke et al., 1994; Lewis, 1987; Belanger and Mikutel, 1985; Lee, 1977). However, Chadwick et al. (1999) have modified the traditional seepage meter to measure the concentration and fluxes of VOCs (primarily TCE, 1,2-dichloroethene (DCE), 1,1-DCE, and vinyl chloride (VC) migrating out of the sediment. Instead of a single sampling bag, a multiport sampling configuration was used. The system incorporated two rotary selector valves that allowed attachment of six sample bags. A control system attached to the valves allowed sampling at pre-selected intervals.

Applications and Limitations

Seepage meters have been used to measure nutrient and contaminant concentrations from groundwater seepage in many different environments, including the deep sea (Linke et al., 1994), coral reefs (Lewis, 1987), lakes (Belanger and Mikutel, 1985; Lee, 1977), and bays (Chadwick et al., 1999). Seepage meters are an excellent measurement tool for groundwater seepage; however, measurements of nutrient concentrations may be questionable if anaerobic conditions are allowed to occur in the enclosed portion of the cylinder (Belanger and Mikutel, 1985). This condition greatly enhances the release of nutrients from the sediment, thus overestimating the actual concentrations present in sediment pore water.

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14. ABSTRACT
Growing evidence suggests that submarine groundwater discharge may represent an important migration pathway for natural and anthropogenic constituents entering coastal waters. To address this issue, a series of technologies were investigated for their applicability toward direct quantification of coastal contaminant migration via groundwater. Technologies were divided into two categories: (1) technologies for quantifying groundwater flow to coastal waters, and (2) technologies for detecting contaminants in the groundwater–coastal water exchange zone. The technologies evaluated for quantifying groundwater flow to coastal waters include seepage meters, thermal gradient flow meters, piezometers, thermal infrared aerial imagery, tracer injection, a colloidal borescope, and natural geochemical tracers. The technologies for detecting contaminants in the groundwater–coastal exchange zone include porewater probes, mini-wells, diffusion samplers, seepage meters, and in situ chambers. A matrix was developed to evaluate these technologies. The factors for consideration of each technology include technical performance/applicability, developmental status, reliability, and cost. A panel of experts will fill out the matrix and the selected technologies will then be evaluated for a demonstration based on the panel results.

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